

# **A Model to Estimate and Predict the Surface Tension and Surface Concentration of Liquid Mixtures**

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## **Abstract**

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This work presents a model to estimate surface tension and surface concentration of liquid binary systems, which includes the non-ideality of the liquid bulk phase and the surface layer through the calculation of activity coefficients, using the UNIFAC group contribution model. The calculation method used to estimate the quantities above mentioned makes an analogy between pressure and vapor concentration from a traditional bubble point calculation and the surface tension and surface concentration, respectively. In order to test the model and calculation method here proposed, values for the surface tension of binary mixtures were calculated for the following systems: benzene + nitrobenzene, n-hexadecane + n-eicosane, n-pentane + butanenitrile and isobutanol + n-decanol, at different temperatures, in the whole concentration range. Simultaneously, values of the surface concentration for the same binary systems were also obtained. The average relative error obtained from the comparison of experimental and calculated surface tension values for the above mentioned binary systems was only 0.69 % which takes us to establish that the model, together with the calculation scheme here proposed are highly reliable.

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**Key words:** Surface tension, surface concentration, binary systems, calculation, bubble point, UNIFAC.

## **Introduction**

Surface tension is one of the most interesting thermophysical properties due to its manifestation in many of the naturally occurring phenomena as well as in many industrial applications. Surface effects have high industrial importance, i.e., many reactions occur easily over the surface of a catalyst, and this fact makes heterogeneous catalysis important in many industrial applications. Moreover, processes like lubrication, corrosion, adherency, detergency, and reactions in electrochemical cells are also related to surface effects. In fact, liquid-vapor interfaces are critical to the performance of detergent and soaps, to chemical engineering separation processes such as absorption and distillation, to petroleum recovery, and to the function of biological membranes, to mention just a few examples.

As part of a systematic work on surface tension, which includes experimental determination and calculations, carried out by our research group [1-4] for pure and mixed organic liquids of interest in the oil industry, this work presents a model and calculation method to predict mixture surface tension values, tested here for binary systems. The model and calculation method presented in this work are extended in a straightforward manner to multicomponent mixtures, this fact has already been explored and the results obtained will be the subject of a separate work [5].

The model used to calculate surface tension for binary systems, is that originally proposed to calculate the surface layer concentration from the corresponding mixing Gibbs energy for both the liquid bulk and the surface layer, which has been well documented [6-8].

The calculation method used to derive mixture surface tension and surface layer concentration is similar to that extensively used for bubble point calculations. The contribution in this respect is the analogy used between the bubble point pressure and vapour concentration with surface tension and surface concentration, respectively. In some way, the problem of representing the thermodynamic equilibrium between liquid bulk and the surface layer is taken as that between liquid bulk and vapour as if the former were the only phases present. Furthermore, activity coefficients for both the liquid bulk and the surface layer are derived using the UNIFAC [10, 11] group contribution model during the iterative process to fulfill the equilibrium constraints used.

The binary systems included in this study to test the model and the calculation method, are representative of different type of mixtures: polar + polar, non-polar + non-polar, non-polar + polar. The systems are: benzene + nitrobenzene, n-hexadecane + n-eicosane, n-pentane + butanenitrile and isobutanol + n-decanol, at different temperatures, in the whole concentration range.

### **Thermodynamic Relationships**

Most of the fundamental thermodynamic relationships used to describe the mixing Gibbs energy function for both the liquid bulk and the surface layer which in turn are used to derive the equations that allow the calculation of the surface concentration are well documented [6-8]. For the purposes of the present work, only the expressions for the

calculation of both the surface tension and surface concentration for a binary system are included, for component 1:

$$x_1^s = \frac{x_1 g_1}{g_1^s} \exp \left[ \frac{\Omega_1 (s - s_1)}{RT} \right] \quad (1)$$

and for component 2:

$$x_2^s = \frac{x_2 g_2}{g_2^s} \exp \left[ \frac{\Omega_2 (s - s_2)}{RT} \right] \quad (2)$$

In the two previous equations,  $x$ , is the mole fraction;  $\gamma$ , is the activity coefficient;  $\sigma$ , is the surface tension;  $\Omega$ , is the molar surface area evaluated according to equation (3); quantities with  $\sigma$  as superscript correspond to the surface layer whereas those without superscript correspond to the liquid bulk; and subscripts 1 and 2 correspond to the components of the binary mixture.

The molar surface area for each component is evaluated using the following relation [9]:

$$\Omega_i = (V_{mi})^{2/3} (N_A)^{1/3} \quad (3)$$

where,  $V_{mi}$ , is the molar volume for component  $i$ , and  $N_A$ , Avogadro's constant.

The activity coefficients which take into account the non-ideality of both the liquid bulk and surface layer can be determined by employing any of the well known activity coefficient models. In this work, the UNIFAC group contribution activity coefficient model [10, 11, 14] has been used due to the availability of interaction parameters for the molecular groups involved in the systems included to test the method.

### Calculation Method

The algorithm used in this work to carry out the simultaneous calculation of surface tension ( $\sigma$ ) and surface concentration ( $x_i^\sigma$ ) is similar to that used in isothermal bubble point calculations for systems showing vapour-liquid equilibria [12], where a physical equilibrium constant relating the concentration of the liquid and vapor phases is introduced. In an analogous way, an equilibrium constant relating the liquid bulk and the surface phase concentration is introduced, according to:

$$K_i^\sigma = x_i^\sigma / x_i \quad (4)$$

The following constraint is also included:

$$x_1^s + x_2^s = 1 \quad (5)$$

thus, the following relation also holds:

$$\sum x_i K_i^\sigma = 1 \quad (6)$$

In fact, equation (6) is considered in the convergence criteria during the search for the best values for  $\sigma$  and  $x_i^\sigma$ , the mixture surface tension and the surface concentration, respectively.

The objective function used to derive the surface tension for the mixture, during the inner iterative process in the bubble pressure like algorithm used, has the following form:

$$f(\sigma) = \frac{x_1 \gamma_1}{\gamma_1^\sigma} \exp\left[\frac{\Omega_1(\sigma - \sigma_1)}{RT}\right] + \frac{x_2 \gamma_2}{\gamma_2^\sigma} \exp\left[\frac{\Omega_2(\sigma - \sigma_2)}{RT}\right] - 1 = 0 \quad (7)$$

To solve equation (7), the Newton-Raphson method is used to obtain the mixture surface tension value; the  $n+1$  approximation for  $\sigma$  is evaluated according to the following expression:

$$\sigma^{n+1} = \sigma^n - \frac{f(\sigma^n)}{f'(\sigma^n)} \quad (8)$$

The Newton-Raphson method needs a first approximation for  $\sigma$  to initiate the iterative process for finding the best value of the mixture surface tension, in this work the following relation has been used to obtain such approximation

:

$$\mathbf{S}_n = x_1 \mathbf{S}_1 + x_2 \mathbf{S}_2 \quad (9)$$

It should be mentioned that a similar derivation of the corresponding equations can be performed for multicomponent systems [5].

## Results and discussion

In order to test the model proposed to calculate surface tension and surface concentration values, the following different type of binary systems, were selected:

Aromatic + Substituted Aromatic: Benzene + Nitrobenzene [13]

Non-Polar + Non-Polar: n-Hexadecane + n-Eicosane [1]

Non-Polar + Polar : n-Pentane + Butanenitrile [2]

Polar + Polar: Isobutanol + n-Decanol [15]

Table 1 shows the calculated results for the binary system Benzene + Nitrobenzene, at 293.15 and 303.15 K. The different columns of this table show: component 1 liquid bulk concentration, bulk activity coefficients for components 1 and 2, component 1 surface

concentration, surface activity coefficients for components 1 and 2, experimental and calculated mixture surface tension values and the point to point relative error. The experimental values taken from Suri and Ramakrishna [13] are the liquid bulk concentration and mixture surface tension values. The remaining values included in Table 1 correspond to those obtained with the proposed method, i.e., activity coefficients for both the liquid bulk and the surface evaluated using the UNIFAC model, together with binary group interaction parameters from Gmehling et al. [11] and Bastos et al. [14], the calculated mixture surface tension values, and the relative error in % for each point.

Figure 1 shows graphically the experimental and calculated surface tension values as a function of concentration, at 293 and 303 K for the binary system benzene + nitrobenzene, in this figure symbols are used to represent the experimental values, and full lines represent the calculated surface tension values. From this figure it is possible to observe the high accuracy of the calculated surface tension values as a function of concentration at the different temperatures. Figures 2 to 4 show graphically a comparison between experimental and calculated surface tension data for the binary systems: n-hexadecane + n-eicosane, n-pentane + butanenitrile, and isobutanol + n-decanol, respectively, at different temperatures as indicated in each figure. From these figures, it is obvious that the reproducibility of the corresponding experimental behavior, as a function of concentration and temperature is adequately reproduced by the model and calculation method reported in this work.

Table 2 includes the global statistics for the four binary systems used to test the model and calculation method proposed. From Table 2 it is possible to mention that there exists a point



with an error of 3.79%, and occurs in the binary n-pentane + butanenitrile, at 293.15 K, which can be considered the worst case. A possible explanation of this difference could be that this system shows large deviations with respect to ideality because of the different chemical nature of the components. Nonetheless, according to the differences between experimental and calculated surface tension values, the method here proposed to estimate surface tension values for binary systems reproduces very well the experimental surface tension-concentration behavior for the four binary systems included in this work.

In addition to the estimation of mixture surface tension, the surface concentration is also obtained, simultaneously, using the isothermal bubble point like iterative procedure proposed in this work. However, calculated surface concentration data can not be compared with experimental values because of the lack of this type of information. Figures 5 and 6 present calculated results of surface concentration plotted against liquid bulk concentration at two temperatures, for n-Hexadecane + n-Eicosane and n-Pentane + Butanenitrile, respectively. Figures 5 and 6 clearly show the degree in which the calculated surface concentration data diverge from the bulk concentration, which is a clear indication of the tendency of component 1, the most volatile component in the two systems considered, to travel to the surface layer, that is, the tendency to preferential surface adsorption. The surface concentration, as obtained here, will be the subject of future work to determine its relation to different processes of scientific and practical interest.

## **Conclusions**

The thermodynamic model together with the calculation method here proposed to estimate mixture surface tension and surface concentration values is able to reproduce within experimental uncertainty, the experimental surface tension behavior as a function of concentration and temperature, for different types of binary systems as established by the average absolute relative percent error obtained with the 86 experimental points considered in this study, which was 0.69%.

It is clear that the model and calculation method developed here can be used for the prediction of surface tension values of binary systems, both as a function of concentration and temperature, without the use of any adjustable parameter.

Furthermore, there exists the possibility of using the surface concentration, as obtained in this work, to establish the selective adsorption of a given component in liquid-vapor interfaces.

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Table 1. Results of the prediction of surface tension and concentration for the binary system benzene (1) + nitrobenzene(2).

T=293.15 K								
$x_1^{[13]}$	$\gamma_1$	$\gamma_2$	$x_1^\sigma$	$\gamma_1^\sigma$	$\gamma_2^\sigma$	$\sigma_{\text{exp}}^{[13]}$ (mNm <sup>-1</sup> )	$\sigma_{\text{cal}}$ (mNm <sup>-1</sup> )	%E
0.0000	1.1958	1.0000	0.0000	1.1958	1.0000	43.40	43.40	
0.1152	1.1749	1.0011	0.2717	1.1456	1.0073	40.72	40.92	0.49
0.2003	1.1591	1.0037	0.4268	1.1154	1.0221	39.13	39.26	0.33
0.3335	1.1338	1.0119	0.6127	1.0765	1.0636	36.97	36.91	-0.15
0.4254	1.1157	1.0219	0.7101	1.0546	1.1076	35.68	35.46	-0.62
0.5333	1.0935	1.0412	0.7995	1.0340	1.1781	34.25	33.91	-1.01
0.6320	1.0722	1.0705	0.8623	1.0199	1.2612	33.01	32.63	-1.17
0.7285	1.0504	1.1190	0.9094	1.0104	1.3580	31.75	31.50	-0.79
0.8177	1.0299	1.1984	0.9436	1.0047	1.4592	30.78	30.57	-0.70
0.9117	1.0099	1.3637	0.9732	1.0012	1.5814	29.67	29.67	0.00
1.0000	1.0000	1.7341	1.0000	1.0000	1.7341	28.85	28.85	
T=303.15 K								
$x_1^{[13]}$	$\gamma_1$	$\gamma_2$	$x_1^\sigma$	$\gamma_1^\sigma$	$\gamma_2^\sigma$	$\sigma_{\text{exp}}^{[13]}$ (mNm <sup>-1</sup> )	$\sigma_{\text{cal}}$ (mNm <sup>-1</sup> )	%E
0.0000	1.1763	1.0000	0.0000	1.1763	1.0000	42.20	42.20	
0.1152	1.1588	1.0009	0.2668	1.1346	1.0061	39.15	39.72	1.43
0.2228	1.1418	1.0040	0.4551	1.1021	1.0232	37.05	37.64	1.57
0.3335	1.1235	1.0103	0.6042	1.0735	1.0546	35.43	35.71	0.79
0.4374	1.1053	1.0208	0.7132	1.0509	1.0996	34.07	34.07	0.00
0.5333	1.0874	1.0368	0.7926	1.0337	1.1569	32.82	32.69	-0.40
0.6320	1.0679	1.0636	0.8568	1.0200	1.2328	31.65	31.39	-0.81
0.7285	1.0476	1.1086	0.9057	1.0105	1.3226	30.61	30.25	-1.18
0.8217	1.0274	1.1870	0.9427	1.0046	1.4226	29.58	29.26	-1.10
0.9118	1.0094	1.3369	0.9722	1.0012	1.5343	28.54	28.38	-0.55
1.0000	1.0000	1.6791	1.0000	1.0000	1.679	27.55	27.55	

Table 2. Global statistics of the comparison of mixture surface tension for the four binary systems included in this study.

Binary	Number of points	T/K	max rel error  %	ave rel error  %
Benzene + Nitrobenzene	11	293.15	1.17	0.48
	11	303.15	1.57	0.71
n-Hexadecane + n-Eicosane	9	323.15	0.49	0.23
	9	333.15	0.43	0.16
	9	343.15	0.61	0.14
	9	353.15	0.71	0.35
n-Pentane + Butanenitrile	9	293.15	3.79	1.50
	9	303.15	3.36	1.19
Isobutanol + n-Decanol	10	303.15	2.36	1.49

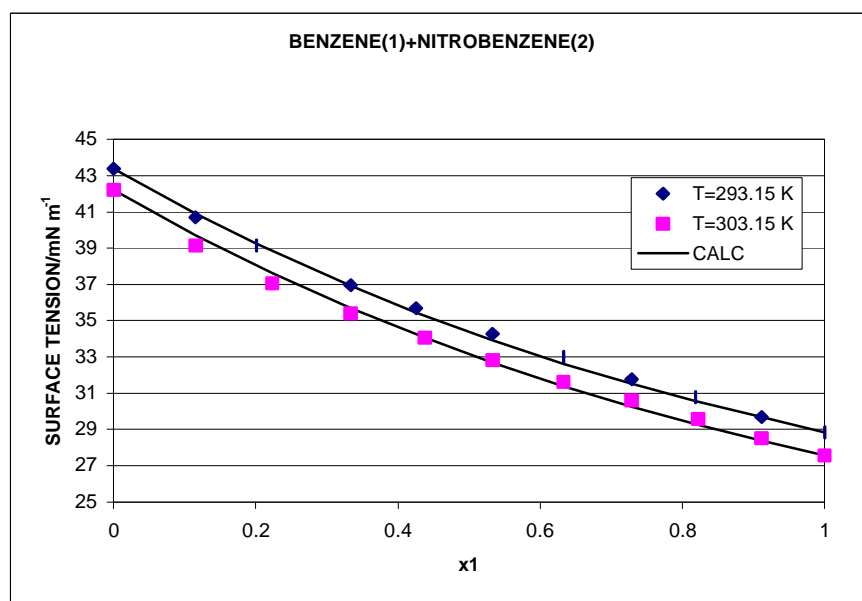


Figure 1. Surface tension vs component 1 liquid bulk concentration, experimental (symbols) and calculated (full line) values for the binary system: Benzene(1) + Nitrobenzene(2), at 293.15 and 303.15 K.

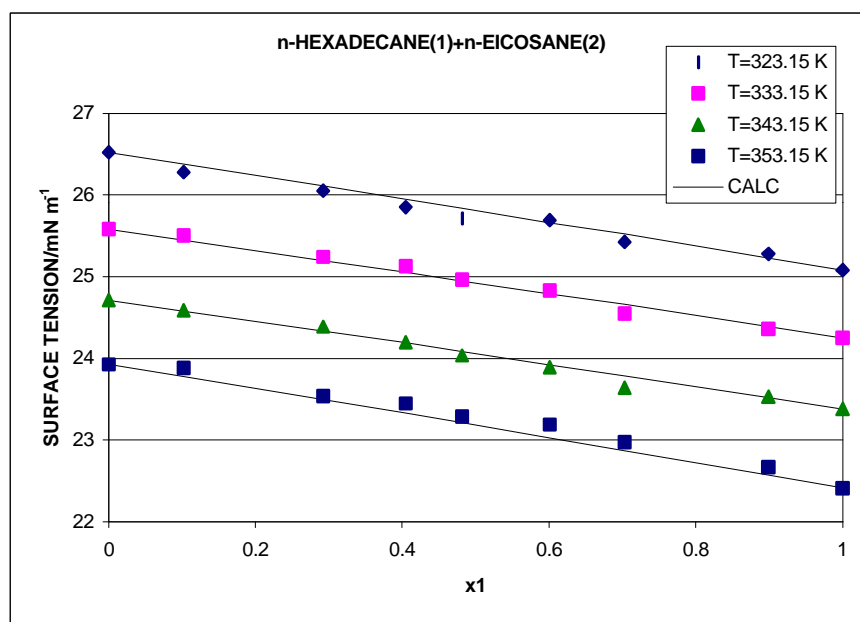


Figure 2. Surface tension vs component 1 liquid bulk concentration, experimental (symbols) and calculated (full line) values for the binary system: n-Hexadecane(1) + n-Eicosane(2), at 323.15, 333.15, 343.15 and 353.15 K.

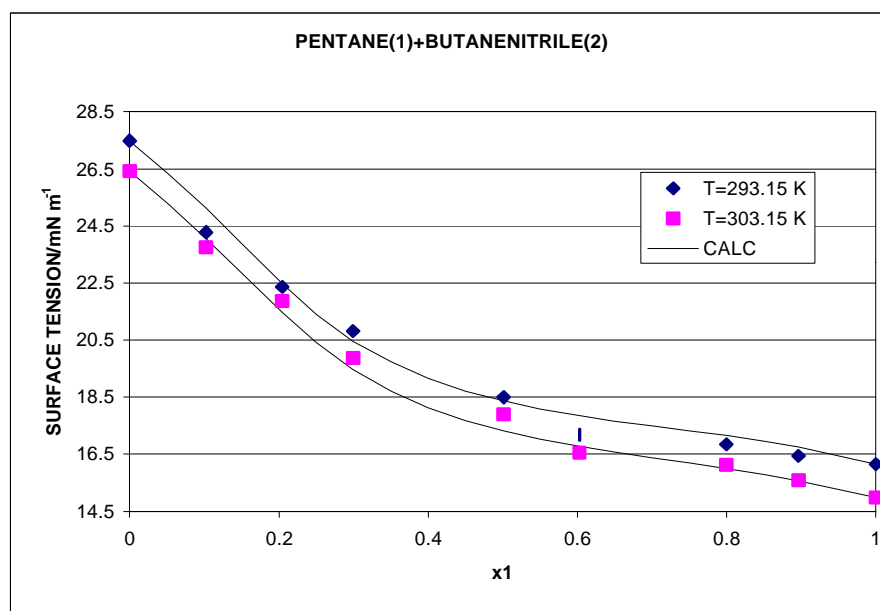


Figure 3. Surface tension vs component 1 liquid bulk concentration, experimental (symbols) and calculated (full line) values for the binary system: n-Pentane(1) + Butanenitrile(2), at 293.15 and 303.15 K.

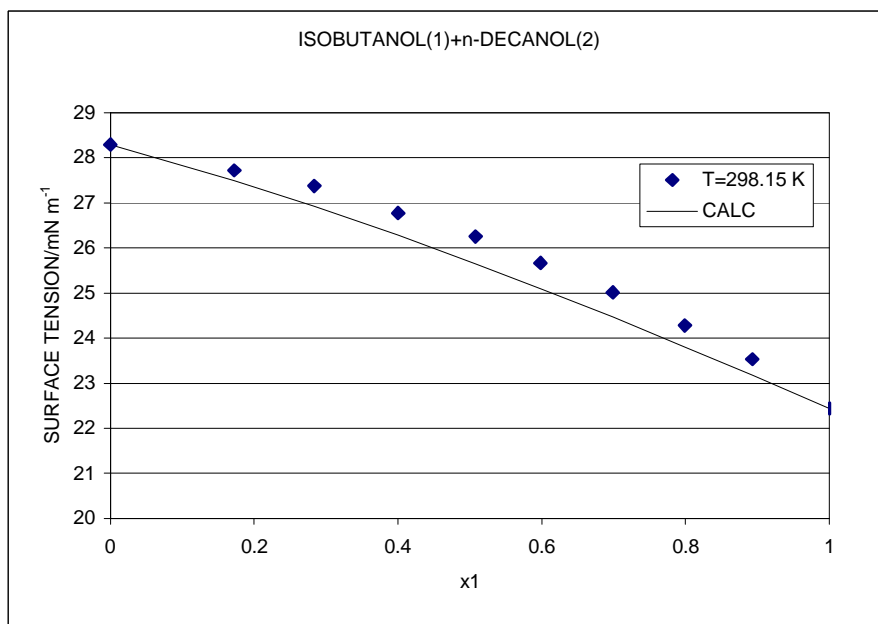


Figure 4. Surface tension vs component 1 liquid bulk concentration, experimental (symbols) and calculated (full line) values for the binary system: Isobutanol(1) + n-Decanol(2), at 298.15 K.



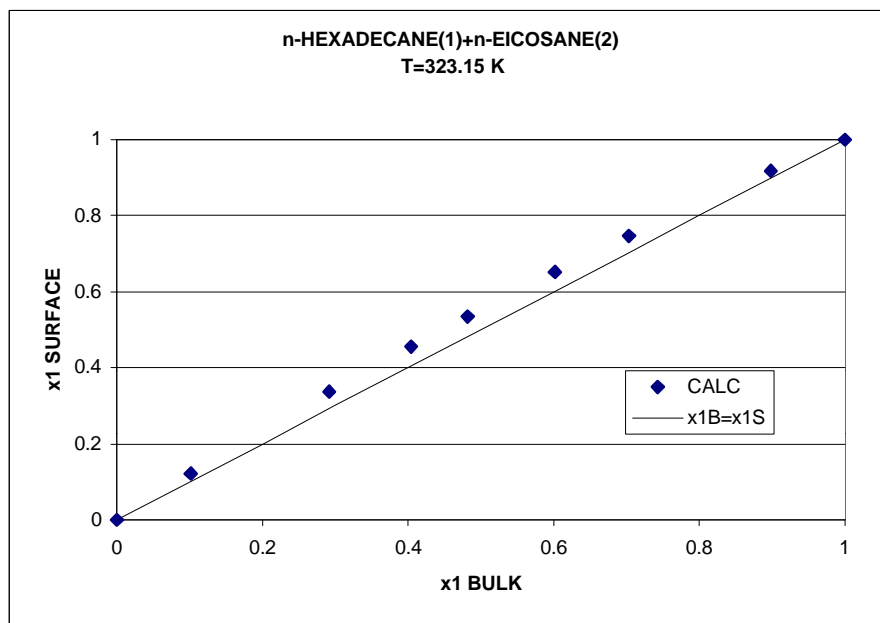


Figure 5. Component 1, mole fraction in the surface vs mole fraction in the liquid bulk for the binary system n-Hexadecane(1) + n-Eicosane(2), at 323.15 K

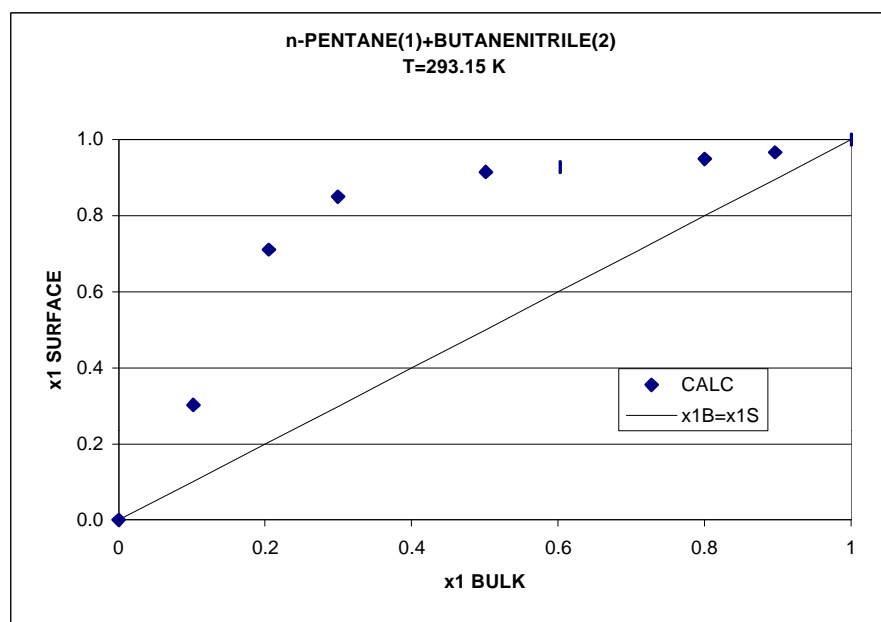


Figure 6. Component 1, mole fraction in the surface vs mole fraction in the liquid bulk for the binary system n-Pentane(1) + Butanenitrile(2), at 293.15 K